Siderite (FeCO₃): Thermal Decomposition in Equilibrium with Graphite

Abstract. *The thermal stability of siderite (FeCO₃) was studied by two independent methods in which the oxygen fugacity of the gas phase was controlled by equilibration with graphite. Both series of experiments indicate that siderite decomposes stably to magnetite + graphite between 455° and 465°C at 500 to 2000 bars $P_{CO_2} + P_{CO}$.*

The thermal decomposition of divalent carbonates may be expressed by two distinct types of reactions (1), where R represents the cation.

$$R CO_3 = RO + CO_2 \qquad (1)$$
$$a RCO_3 + 1/2 O_2 = R_aO_{a+1} + a CO_2 \qquad (2)$$
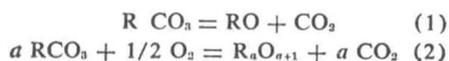
The stabilities of such minerals as calcite ($CaCO_3$), magnesite ($MgCO_3$), and smithsonite ($ZnCO_3$), whose cations do not oxidize during reaction, have been determined (2, 3). However, the carbonates siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) may decompose by reactions of the second type, in which a variety of oxides may form. For this reason, the oxygen fugacity, f_{O_2}, must be controlled in studying decomposition of these carbonates.

We describe here the results of two independent sets of experiments, one performed by each of us, on the stability and decomposition relations of siderite ($FeCO_3$), in which the value of f_{O_2} was controlled by equilibration of the gas phase, composed of CO_2 and CO, with graphite (4, 5).

In both series of experiments, siderite samples were contained in externally heated Tuttle-type cold-seal pressure vessels; carbon dioxide was supplied by an external pumping system (2). In the earlier experiments of Rosenberg (6), samples of synthetic siderite were contained in small sealed gold capsules; during heating, the siderite decomposed slightly, producing an internal pressure equal to that applied on the tube by the external atmosphere (7). In French's later study of siderite stability (8), decomposition relations were determined at values of f_{O_2} controlled by solid-phase oxygen buffer assemblages (5, 9). Synthetic siderite samples contained in open silver tubes were surrounded by the solid buffer; diffusion of the gas phase through the buffer established equilibrium, and the value of f_{O_2} could be calculated directly.

The two types of experiments were carried out independently; comparison of results did not occur until the later study (8) had been completed. In both experiments, siderite was synthesized by decomposition of ferrous oxalate dihydrate ($FeC_2O_4 \cdot 2H_2O$) to siderite and gas at total pressures of 2000 bars and temperatures from 350° to 380°C.

In the sealed-tube experiments (6) there was no intrinsic method for control of oxygen fugacity. However, oxygen buffering was apparently established by the precipitation of graphite or amorphous carbon from the gas phase in the sealed tubes during the experiments. The duration of individual runs varied from 2 to 10 days.

The decomposition of siderite to magnetite within a sealed tube proceeds as follows:

$$3 FeCO_3 = Fe_3O_4 + 2 CO_2 + CO \qquad (3)$$
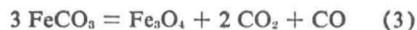
Ideally, the gas phase produced would have a CO_2 to CO ratio of 2; however, such a ratio is metastable with respect to the formation of graphite between 400° and 600°C (4). Thus, graphite would precipitate from the gas phase by the reaction

$$2 CO = C_{(gr)} + CO_2 \qquad (4)$$

Small but significant amounts of black carbonaceous material formed within the sealed tubes during the experiments (6). The exact nature and degree of crystallinity of the material could not be determined because of its scarcity. However, x-ray diffraction studies of similar material precipitated within the pressure vessel in subsequent studies (8) indicate disordered graphite.

Production of graphite within the sealed tube will produce internal buffering of f_{O_2} by equilibria established between graphite and the gas phase (4, 5). At a fixed value of P_{gas} (that is, $P_{CO_2} + P_{CO}$) the temperature at which siderite decomposes will correspond to that of the four-phase assemblage, siderite + magnetite + graphite + gas. In the three-component system, Fe-C-O, the phase rule indicates that this assemblage will be isobarically univariant. The decomposition of siderite to magnetite therefore defines a unique equilibrium temperature if, and only if, graphite is also present in the assemblage. However, reversibility of the reaction (that is, formation of siderite from magnetite) was not directly demonstrated by the sealed-tube method.

Determination of decomposition temperatures by the sealed-tube method was hampered in that some siderite decomposes below the true equilibrium temperature, producing the necessary internal pressure. Traces of magnetite (less than 5 percent of the sample volume) were attributed to such decomposition within the siderite stability field, while production of relatively large amounts of magnetite (more than 20 percent) was evidence that the decomposition temperature of siderite had been exceeded (6).

In subsequent experiments with buffered siderite samples in open tubes (8) for an independent determination of the decomposition temperatures, the buffer mixture consisted of graphite to which magnetite had been added; buffering was accomplished by the graphite alone. Reversibility of the equilib-

Table 1. Estimated decomposition temperatures for siderite in equilibration with graphite. $P_{gas} = P_{CO_2} + P_{CO}$.

P_{gas} (bars)	Sealed tubes (6)		Open tubes, buffered (8)	
	T (°C)	$-\log f_{O_2}$*	T (°C)	$-\log f_{O_2}$
500	452	25.9	455	25.7
1000	454	25.4	458	25.2
2000	463	24.5	465	24.4

* Values of $\log f_{O_2}$ calculated for the graphite + gas buffer (5), corrected for the effect of pressure on the solid phase.